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IDENTIFICATION OF CORROSION PRODUCTS AND CORROSION PROCESSES OF ACSR CONDUCTORS

Report No 90-113-K

K.S. Yoshiki-Gravelsins and H. Leung
Environmental Science Section
Chemical Research Department

ABSTRACT

A test procedure involving x-ray diffraction analysis, scanning electron microscopy with energy dispersive x-ray analysis facilities, and other spectroscopic techniques (x-ray fluorescence, Auger spectroscopy) has been used in the identification of corrosion products of ACSR transmission line conductors from three sites: Port Colborne, Guelph, and Smiths Falls. Aluminum strands exposed to industrial environments (Port Colborne, Guelph) for greater than 45 years form amorphous aluminum sulphates and chlorides. Aluminum wires exposed to rural environments (Smiths Falls) show no evidence of corrosion other than a passivating layer of aluminum oxide, approximately 1 μm thick. Galvanized steel wires which are sheathed by aluminum strands form amorphous hydroxysulphates in both rural and industrial environments; however, amorphous chlorides are present only in industrial environments. The results of this study support a corrosion mechanism in which oxide-covered aluminum adsorbs reactive anions and undergoes localized pitting. Zinc, on the other hand, is readily oxidized to zinc hydroxide, and mixed salt hydrozincites in the presence of CO_2. Further reaction with pollutant constituents, under changing acidic conditions, results in product dissolution and precipitation of other zinc salts.

job	file	date	report no.
35-104-431	825.154	May 18, 1990	90-113-K

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EXECUTIVE SUMMARY

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K.S. Yoshiki-Gravelsins and H. Leung
Environmental Science Section
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By the end of the century, more than one-third of Ontario Hydro's transmission network will be older than 50 years. The objective of the transmission line refurbishment programme is to estimate the useful life of transmission system components, and to establish the costs, schedules and priorities for the first set of candidate lines to be refurbished. To this end, the Environmental Science Section is investigating the environmental conditions which contribute to atmospheric corrosion of transmission line conductors, and establishing the relationship between conductor life and air pollutant concentrations. Knowledge of the chemical and physical nature of corrosion products is essential in identifying key environmental parameters in the corrosion process and in determining the mechanisms by which corrosion takes place. The presence of both amorphous aluminum hydroxysulphates and chlorides and amorphous zinc hydroxysulphates and chlorides, on the surfaces of highly corroded conductor line samples, confirms that chloride and sulphate pollutants are corrosive towards these metals. In addition, these species contribute to the overall conductivity of the surrounding electrolyte. Electrolyte properties are further affected by temperature, relative humidity, and chemical composition, each of which influences the wetting behaviour of the electrolyte. Surfaces which exhibit limited corrosion appear to be passivated by basic salts, such as alumina, zincite and zinc hydroxide, which are stable at neutral pH; in acidic media, the corrosion process is dependent on the anion present (eg, Cl^-, SO_4^{2-}). Finally, the chemical composition and surface morphology of the corrosion product layers support the following corrosion mechanisms. Under moist conditions, zinc is oxidized to zinc hydroxide, and in the presence of CO_2 this product further reacts to form zinc hydroxycarbonate or mixed salt hydrozincites (when aluminum is in contact with galvanized steel).

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Reaction with pollutant constituents leads to formation of zinc hydroxysulphates and hydroxychlorides. In acidic media, these products dissolve and precipitation of zinc sulphate occurs. As the pH increases basic salts precipitate which inhibit further corrosion until additional acid is supplied. In the corrosion of aluminum, there is deposition of anions such as SO_4^{2-} or Cl^- on the oxide-covered surface, followed by chemical reaction, and then thinning of the oxide film by dissolution. Corrosion of aluminum is characterized by localized pitting rather than uniform deterioration.

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IDENTIFICATION OF CORROSION PRODUCTS AND CORROSION PROCESSES OF ACSR CONDUCTORS

1.0 INTRODUCTION

1.1 Background

Ontario Hydro's transmission system is aging, and with age the capability of older components to withstand variations in weather conditions, increased levels of pollutants and contaminants, and normal operational loads will be diminished. The introduction of replacement lines and novel overhead line designs will dictate the need for improved information on the remaining life of existing facilities. The Environmental Science Section is participating in the development of an effective refurbishment programme by investigating the environmental conditions which contribute to corrosion of transmission line conductors, and establishing the relationship between conductor life and air pollutant concentrations. In this report, corrosion products and corrosion processes of ACSR conductors are discussed by examination of three line samples from Port Colborne, Guelph and Smiths Falls.

1.2 Objectives

The primary objective of this study is to observe corrosion of ACSR conductors; identify corrosion products; and, to establish a procedure for future analyses of conductor samples. Analysis leads to insight to corrosion mechanisms and to identification of environmental parameters comprising corrosive atmospheres. The results of this study will provide a guideline for determining a correlation between prevailing environmental conditions and degree of corrosion.

2.0 CHARACTERIZATION OF ACSR CONDUCTORS

2.1 Sample Description

Samples of ACSR conductors may be classified by geographical location, the materials and conductor design specifications used, age, existing measures of corrosion intensity, and according to environmental conditions at the installation site. A description of each follows.

2.1.1 Geographical Location

Samples of transmission line conductors were selected from three locations: Port Colborne, Guelph and Smiths Falls with relatively diverse environments. The locations of these sites are indicated in Figure 1.1. There are numerous foundries and chemical and metal processing industries located in the Guelph area. Most notable are Alcan Ingot Alloys (aluminum alloys), in part responsible for SO_2 and NO_x emissions and particulates, Guelph Dolime Ltd. (lime plant), Fiberglas Canada Inc. (synthetic fibres) and Hart Chemical Ltd. (texture finishing chemicals, resins). Port Colborne is the site of Inco Ltd. - Ontario Division Refinery (nickel smelting and refining) and Port Colborne Quarries which manufactures stone products. Smiths Falls is a rural area - the major manufacturer being Hershey Canada Inc. (chocolate products).

In addition, alkali halides are released to the environment by the use of road salt, fertilizers and improper irrigation practices [1].

The lines from Port Colborne and Guelph were known to be highly corroded (based on visual observation and mechanical testing data) unlike the visually clean sample from Smiths Falls.

2.1.2 Materials and Conductor Design Specifications

Transmission line conductors consist of strands of aluminum wound around a core of galvanized steel. The samples from Port Colborne and Smiths Falls were constructed of a centre core of 7 galvanized steel wires and 30 and 26 aluminum wires, respectively, arranged in two layers about the steel core. The sample from Guelph consisted of a single layer of 6 aluminum wires sheathing 7 steel wires. Data on the three types of ACSR conductors are presented in Table 2.1.

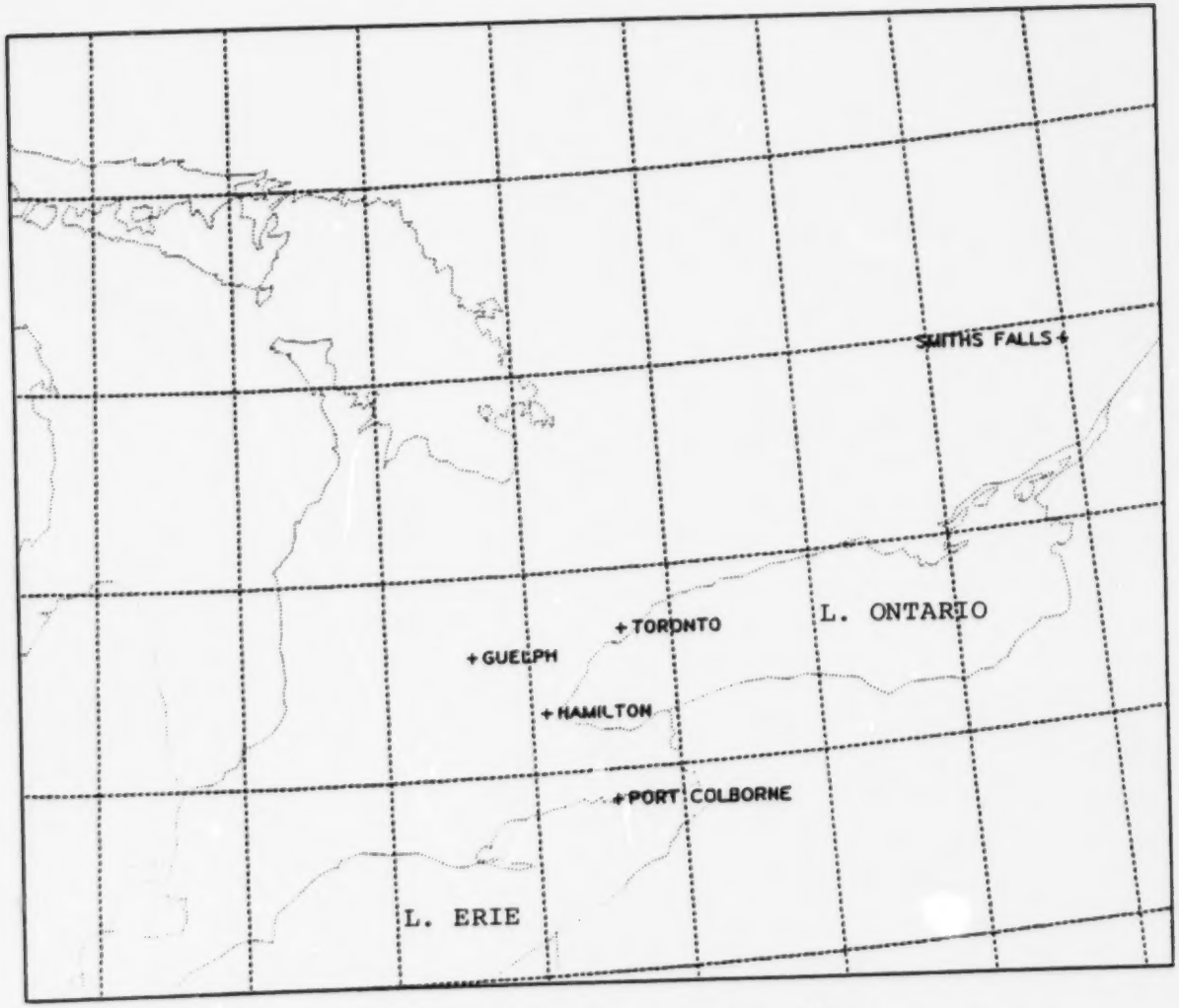


Figure 1.1 Location of Conductor Sites -
Port Colborne, Guelph, Smiths Falls

TABLE 2.1

DESIGN SPECIFICATIONS OF ACSR CONDUCTORS

Location (Stranding)	Outside Dia. in.	Alum. Area sq.in.	Total Area sq.in.	Strand Diameter Alum. in.	Steel in.	Steel Core Dia. in.	Rated Tensile Strength lbs.
Port Colborne (30/7)	.7413	.2642	.3259	.1059	.1059	.3177	17 050
Guelph (6/7)	.633	.2095	.2367	.2109	.0703	.2109	9 545
Smiths Falls (26/7)	.858	.3746	.4356	.1355	.1054	.3162	19 000

2.1.3 Measures of Corrosion Intensity

Existing measures of the degree of corrosion or corrosion intensity are based on changes in mechanical and electrical properties. Detailed descriptions are given elsewhere [2]. Losses in tensile strength and torsional ductility, and Cormon rating (loss of zinc) for the Port Colborne, Guelph and Smiths Falls line conductors are listed in Table 2.2. The ductility data are the average number of turns of outer galvanized steel strands before breakage. Cormon ratings from 1 to 4 represent remaining zinc layer thicknesses of 80-100%, 50-80%, 20-50%, and 0-20%, respectively.

TABLE 2.2

CORROSION INTENSITIES OF GALVANIZED STEEL STRANDS

Conductor Site	Age in years	Remaining Tensile Strength %	Torsional Ductility No. Turns	Cormon Rating
Port Colborne	64.0	69	3.2	N/A
Guelph	46.9	44	11.0	N/A
Smiths Falls	60.8	79	15.8	4

2.1.4 Environmental Conditions

The atmospheric conditions at Port Colborne, Guelph and Smiths Falls or nearby sites, are available in an environmental data base described elsewhere [3] which combines meteorological data (temperature, precipitation, wind, etc.), air quality data (SO_2, NO, NO_2, total suspended particulates, etc.), precipitation chemistry data (pH, SO_4^{2-}, Cl^-, etc.), and emissions data (SO_2, NO_x, alkaline dust, etc.).

TABLE 2.3

SUMMARY OF ENVIRONMENTAL CONDITIONS

	Port Colborne	Guelph	Smiths Falls
SO_2 Concentration (ppm): 1985	0.007	0.003	0.002
Soiling Index (COHS/1000 ft) (COHS=Coefficient of Haze)	0.24	0.3	0.14
Total Suspended Particulates (TSP) ($\mu g/m^3$)	57	73	39
Sulphate in TSP ($\mu g/m^3$)	7.1	4.8	6.9
pH	4.30*	4.34	4.46
Chloride in Precipitation (mg/L)	-	0.232	0.184
Sulphate in Precipitation (ppm)	8.34*	3.30*	2.45*
Relative Humidity (%)	72	77	75

* results of field study over 2-week period

In addition, field studies have been conducted at the three sites [4: Ontario Hydro Research Division Report C89-85-K] to complement the existing environmental data base and to determine the extent of local concentration effects in areas nearby environmental monitoring stations. A summary of the environmental conditions, to date, is presented in Table 2.3.

2.2 Methods of Chemical Analysis

A variety of analytical methods were employed to identify the elements, crystalline compounds, and cross-sectional distribution of elements of the corroded line conductor samples. A brief description of the analytical techniques and the information derived is given below.

2.2.1 X-Ray Fluorescence

X-ray fluorescent analysis is a technique whereby characteristic spectra are excited when a specimen is irradiated with a beam of short-wavelength x-rays. Intensities of the resulting fluorescent x-rays are proportional to the number of excited atoms.

The surfaces of the inner and outer aluminum strands and galvanized steel strand of each conductor sample were scraped and analyzed. The elements detected (Table 2.4) are arranged in decreasing order of concentration from main constituent to trace amount.

TABLE 2.4

X-RAY FLUORESCENCE RESULTS

Conductor Sample	Main	Major	Minor	Trace
Outer Aluminum				
Port Colborne	Al Zn	S	Si Ni P Fe	Cu Pb As Co
Guelph		Al Fe Zn	Si S	Cu K Ca Mn Ti Ni Pb As
Smiths Falls		Al Fe	Si Zn	Cu K Ca Mn Ti
Inner Aluminum				
Port Colborne	Al Zn	Fe Ni	S	Cu Si
Smiths Falls		Al Fe Zn Si	Ca K	Cu Mn Ti Ni S P
Galvanized Steel				
Port Colborne	Zn	Al Fe	S	Cu Ca Mn Ni P Co
Guelph	Fe	Zn	Al Pb	Cu K Ca Mn S Si
Smiths Falls	Zn	Fe	Si Al	K Ca Mn Ti S P
Loose Deposit				
Port Colborne	Al Zn	Fe Ni	S	Cu Ca Si

2.2.2 X-Ray Diffraction

X-ray diffraction analysis is used for the qualitative identification of crystalline phases. In this method, the condition for diffraction of a beam of x-rays from the planes of a crystal are given by the Bragg equation. Diffraction patterns are specific to a crystalline compound and the crystalline components of a mixture can be identified individually.

X-ray diffraction results of the surface layers scraped from the inner and outer aluminum strands and galvanized steel strands of the three conductor samples are presented in Table 2.5. In addition, loose deposits from the Port Colborne aluminum wires were analyzed.

TABLE 2.5

X-RAY DIFFRACTION RESULTS

Conductor Sample	Crystalline Phases
Outer Aluminum	
Port Colborne	Metallic Aluminum (Al)
	Aluminum Hydroxide/Gibbsite ($Al(OH)_3$)
Guelph	Metallic Aluminum (Al)
	Silicon Oxide (SiO_2)
Smiths Falls	Metallic Aluminum (Al)
	Silicon Oxide/Quartz (SiO_2)
	Feldspars (e.g., $KAlSi_3O_8$)
Inner Aluminum	
Port Colborne	Metallic Aluminum (Al)
	Aluminum Hydroxide/Nordstrandite & Bayerite ($Al(OH)_3$)
Smiths Falls	Silicon Oxide/Quartz (SiO_2)
	Metallic Aluminum (Al)
	Feldspars (e.g., $KAlSi_3O_8$)
Galvanized Steel	
Port Colborne	Zinc Sulphate ($ZnSO_4$)
	Zinc Hydroxide ($Zn(OH)_2$)
	Aluminum Hydroxide ($Al(OH)_3$)
Guelph	Iron Oxide Hydroxide/Goethite ($FeO(OH)$)
	Silicon Oxide/Quartz (SiO_2)
	Feldspars (e.g., $CaAl_2Si_2O_8$)
Smiths Falls	Silicon Oxide/Quartz (SiO_2)
	Zinc Aluminum Carbonate Hydroxide Hydrate ($Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$)
Loose Deposit	
Port Colborne	
Large Particles	Aluminum Hydroxide/Gibbsite & Bayerite ($Al(OH)_3$)
	Nickel Oxide (NiO)
Fine Particles	Aluminum Hydroxide/Nordstrandite ($Al(OH)_3$)
	Calcium Sulphate Hydrate/Gypsum ($CaSO_4 \cdot 2H_2O$)

2.2.3 Auger Spectroscopy

Auger spectroscopy is a surface analytical technique whereby an incident beam of low-energy electrons probes a sample target and the characteristic particles emitted after interaction are detected. Surface analysis results for the outer aluminum strands from Guelph and Smiths Falls, which exhibited black surfaces, are presented in Table 2.6. Identical results were obtained for both samples.

Table 2.6

AUGER SURFACE ANALYSIS RESULTS: OUTER ALUMINUM STRANDS

Conductor Sample	Layer	Carbon	Oxygen	Aluminum	Sulphur
Guelph & Smiths Falls:	Outer Surface	50-66%	20-25%	8-20%	3-6%
	0.1 um Below Surface	10-20%	40-50%	40-50%	< 2%

2.2.4 Leaching

One gram of sample was leached with 10 grams water (one-to-ten gram leach) to determine the presence of fluoride, chloride, nitrate and sulphate in the loose deposit on the outer aluminum strands from Port Colborne (see Table 2.7). The anions were detected by ion chromatography.

TABLE 2.7

LEACHING RESULTS

Conductor Sample	Anions	Weight (µg/g)
Port Colborne (loose deposit)	Sulphate	870
	Chloride	810
	Nitrate	150
	Fluoride	5

2.2.5 Scanning Electron Microscopy - Energy Dispersive X-Ray Analysis (SEM-EDX)

Scanning electron microscopy (SEM) is a technique whereby an electron probe strikes a specimen surface at a given point and gives rise to signals which are collected and amplified. Signals can be collected simultaneously to give information about the entire specimen surface. In x-ray microanalysis, characteristic x-rays are excited from an element and analyzed by energy dispersive means. Various types of output signals are possible including (i) an elemental map where the location of the element possessing the characteristic wavelength is revealed as bright contrast in the image; (ii) a line scan; or (iii) a point analysis where the electron probe is focused on a spot.

Duplicate samples of inner and outer aluminum strands and galvanized steel strands of each conductor were longitudinally cross-sectioned, mounted in epoxy molds and then carbon-coated. All sample cross-sections exhibited thicker corrosion product layers on the surfaces facing the ambient atmosphere. All data correspond to these surfaces unless otherwise indicated. Semi-quantitative analysis of cross-sectioned surface areas was performed as a function of depth below the oxide surface. The results are presented in Tables 2.8a to 2.8c. Since quantitative analysis of light elements is limited, the results have been normalized excluding oxygen. Scanning electron micrographs and corresponding elemental maps are presented in Section 3.0, Interpretation of Results.

TABLE 2.8a

SEM-EDX SEMI-QUANTITATIVE ANALYSIS

OUTER ALUMINUM STRANDS

Port Colborne:

	Depth Below Surface (µm)	Normalized Atomic % Excluding Oxygen							
		Al	S	Cl	Fe	Zn	Ca	Si	Al/S
0-30 µm	0 - 0.500	69	29	2	<1	0	0	-	2.4
(dark	0 - 10	72	27	1	0	<1	0	-	2.7
ridge):	0 - 30	76	23	<1	<1	1	0	-	3.3
	30 - 100	93	6	<1	1	<1	0	-	16
	100 - 150	92	6	0	1	1	<1	-	16
	150 - 200	96	3	0	<1	<1	<1	-	32
below oxide	200 - 210	99	<1	<1	<1	0	<1	-	>100
Interior Surface:	0 - 5	57	12	26	<1	3	2	- Al/Cl =2.2	4.8

Guelph:

	Depth Below Surface (µm)	Normalized Atomic % Excluding Oxygen							
		Al	S	Cl	Fe	Zn	Ca	Si	Al/S
	0 - 5	50	24	3	2	<1	<1	20	2.1
	5 - 20	56	27	4	2	1	<1	10	2.1
	20 - 30	62	25	4	2	<1	1	6	2.5
below oxide	30 - 40	99	<1	0	<1	<1	0	<1	>100
interior	1000	100	0	0	0	0	0	0	-

TABLE 2.8b

SEM-EDX SEMI-QUANTITATIVE ANALYSIS

INNER ALUMINUM STRANDS

Port Colborne:

Depth Below Surface (μm)	Normalized Atomic % Excluding Oxygen					
	Al	S	Cl	Fe	Zn	Ca
0 - 0.250	90	5	1	<1	3	<1
0 - 10	93	4	<1	<1	3	0
0 - 50	92	5	<1	<1	2	<1
50 - 100	93	4	0	<1	3	<1
100 - 200	92	6	<1	1	2	0
200 - 300	95	5	<1	<1	<1	0
<300 (below oxide)	100	0	0	<1	0	0

Smiths Falls:

Depth Below Surface (μm)	Normalized Atomic % Excluding Oxygen					
	Al	S	Cl	Fe	Zn	Ca
0 - 0.250	96	1	<1	3	0	<1
0 - 10	99	<1	<1	<1	0	0

TABLE 2.8C

SEM-EDX SEMI-QUANTITATIVE ANALYSIS

GALVANIZED STEEL STRANDS

Port Colborne:

Depth Below Surface (µm)	Normalized Atomic % Excluding Oxygen			
	Zn	Fe	Cl	S
0 - 50	38	3	27	32
50 - 100	38	5	25	32
100 - 150	37	8	23	32
150 - 200	47	30	18	5
190 - 200	58	19	22	1
<200 (below oxide)	4	94	1	0

Guelph:

Depth Below Surface (µm)	Normalized Atomic % Excluding Oxygen			
	Zn	Fe	Cl	S
0 - 50	9	88	<1	3
150 - 200	14	83	0	3
<200 (below oxide)	1	99	0	<1
spot analysis (within 0-50 µm)	Zn	Fe	Cl	S
	<1	20	79	1

Smiths Falls:

Depth Below Surface (µm)	Normalized Atomic % Excluding Oxygen			
	Zn	Fe	Cl	S
0 - 5 (crust)	70	6	2	22
0 - 30	71	15	<1	14
30 - 50	85	15	<1	<1

3.0 INTERPRETATION OF RESULTS

Corrosion products may be in the forms of dissolved species, and solids including both amorphous and crystalline structures. X-ray diffraction analysis, various spectroscopic techniques and wet chemical methods have enabled identification of minerals, elements and salts and have supported the presence of several amorphous solids within the corrosion product layer. The analysis of these products gives insight to environmental factors critical to atmospheric corrosion of transmission line conductors, and suggests corrosion mechanisms.

3.1 Identification of Corrosion Products

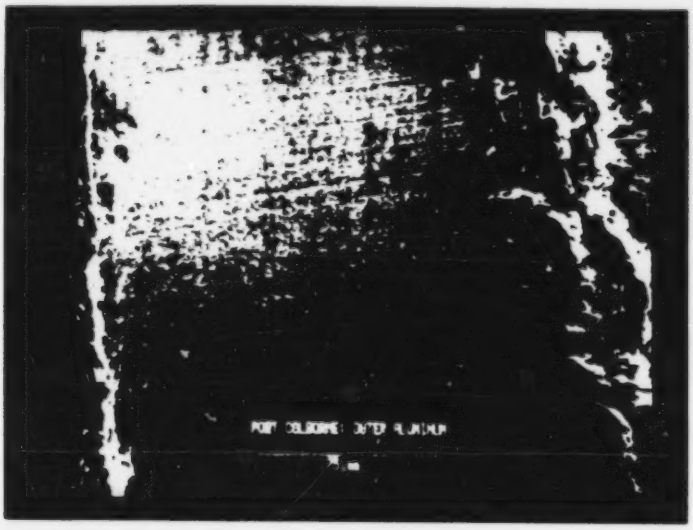
The type of corrosion products present and the surface morphologies of the galvanized steel wires indicate that the relative degree of corrosion of the conductors from the three locations is as follows: Guelph > Port Colborne > Smiths Falls. Scanning electron micrographs and corresponding elemental maps, which follow, show clearly the extent of corrosion of both aluminum and galvanized steel wires.

3.1.1 SEM-EDX Elemental Profiles of Corrosion Layers

3.1.1.1 Outer Aluminum Strands

Aluminum strands from all locations (Port Colborne, Guelph and Smiths Falls) show enhanced corrosion on exterior surfaces facing the ambient atmosphere. Corrosion product layers, 200 μm and 50 μm thick are visible on the SEM micrograph of the longitudinal cross-section of the Port Colborne sample (Figure 3.1a). A view of the 'thicker' layer at higher magnification and corresponding elemental maps are presented in Figures 3.1b and 3.1c, respectively. The corrosion product layer is composed mainly of Al, S and O - $Al(OH)_3$ has been identified by x-ray diffraction and the presence of amorphous $Al_x(SO_4)_y(OH)_z$ is suggested by the results of x-ray fluorescence (XRF) and energy dispersive x-ray analysis (EDX). The Al/S ratio of the concentrated sulphur crust which is approximately 30 μm thick, shown in Figure 3.1c, is Al/S~2. The ratio increases rapidly below the crust to Al/S ~32. Elemental maps of the interior aluminum surface facing the core of the conductor cable are shown in Figure 3.1d. The surface of the sample is on the right side of the micrograph. The composition of this sample is similar to that of the 'thicker' corrosion layer; however, aluminum is present at the surface in bulk concentration and appears to constitute a passivating layer.

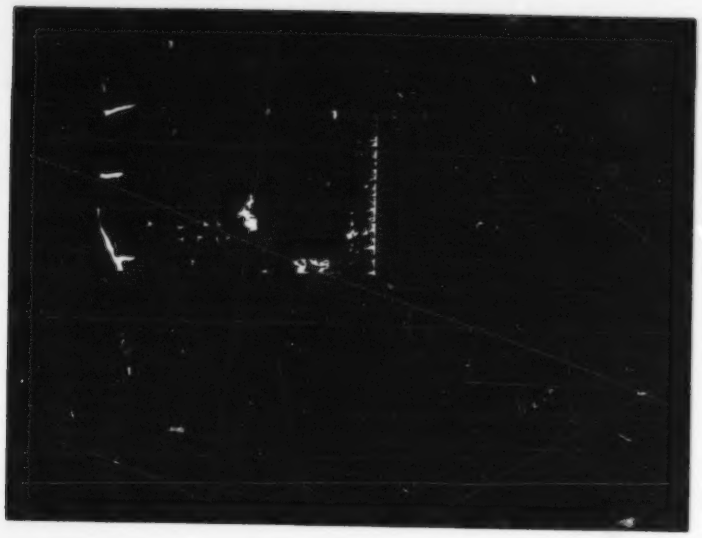
Corrosion is pronounced in the Guelph sample and there is evidence of breakaway (Figure 3.2a). Elemental maps of the corrosion product layer crust (Figures 3.2b and 3.2c) show Al, O, S and Si, as well as Cl in the outermost 5 μm. The source of Si is SiO_2 particulates which have been identified by x-ray diffraction. Analytical results suggest



A

B

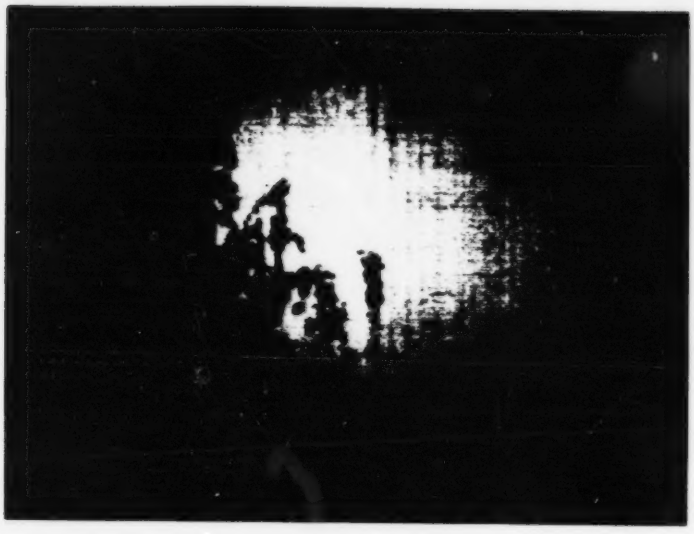
Figure 3.1 Port Colborne: Outer Aluminum Wire
Longitudinal Cross-Section
(a) SEM Micrograph
(b) SEM Micrograph of Exterior Surface



C

D

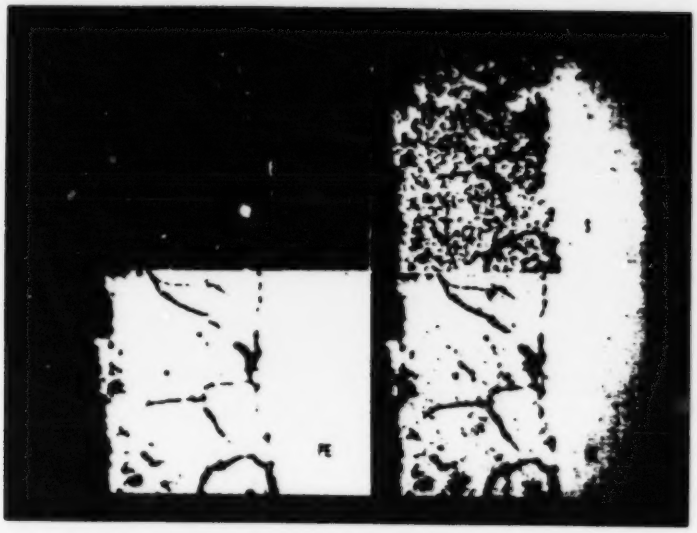
Figure 3.1 Port Colborne: Outer Aluminum Wire
Longitudinal Cross-Section
(c) Elemental Maps (Al,S,O) of Exterior Surface
(d) Elemental Maps (Al,S,O) of Interior Surface



A

B

Figure 3.2 Guelph: Outer Aluminum Wire
Longitudinal Cross-Section
(a) SEM Micrograph of Exterior Surface
(b) Elemental Maps (Al,Cl,O) of
Corrosion Product Layer



C

D

Figure 3.2 Guelph: Outer Aluminum Wire
Longitudinal Cross-Section
(c) Elemental Maps (S,Fe,Si) of Corrosion Product Layer
(d) Elemental Maps (Al,S,O) of Corrosion Product Below Surface

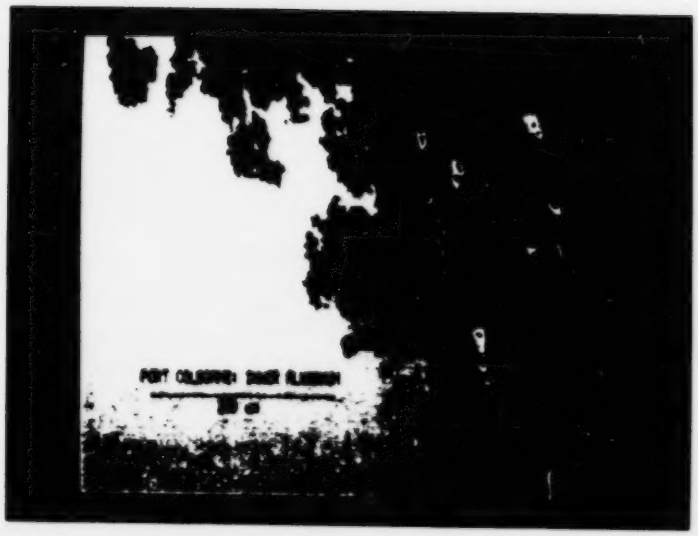


Figure 3.3 Port Colborne: Inner Aluminum Wire SEM Micrograph of Longitudinal Cross-Section

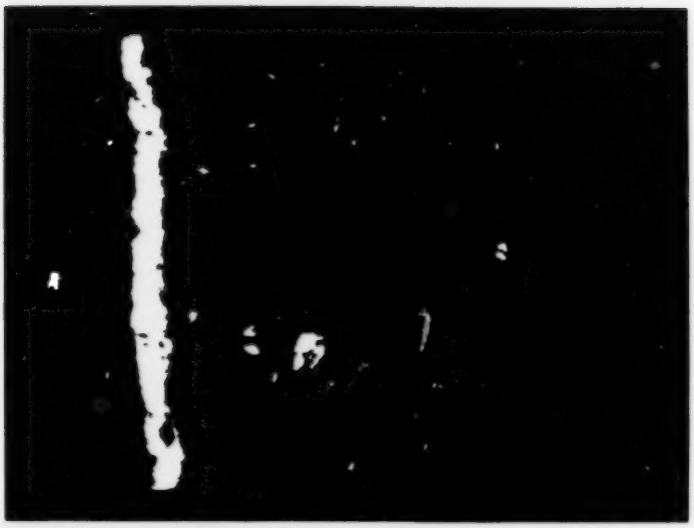
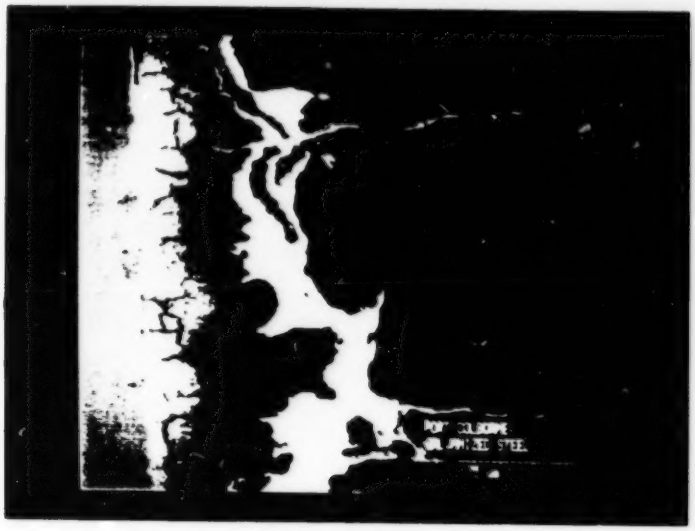
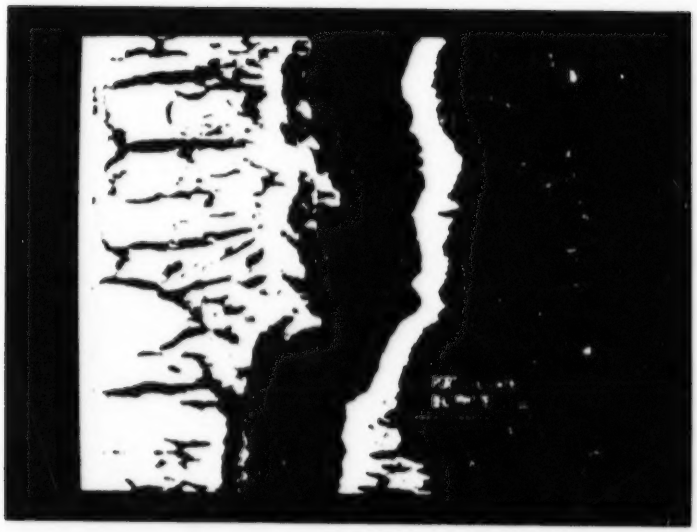


Figure 3.4 Smiths Falls: Inner Aluminum Wire SEM Micrograph of Longitudinal Cross-Section

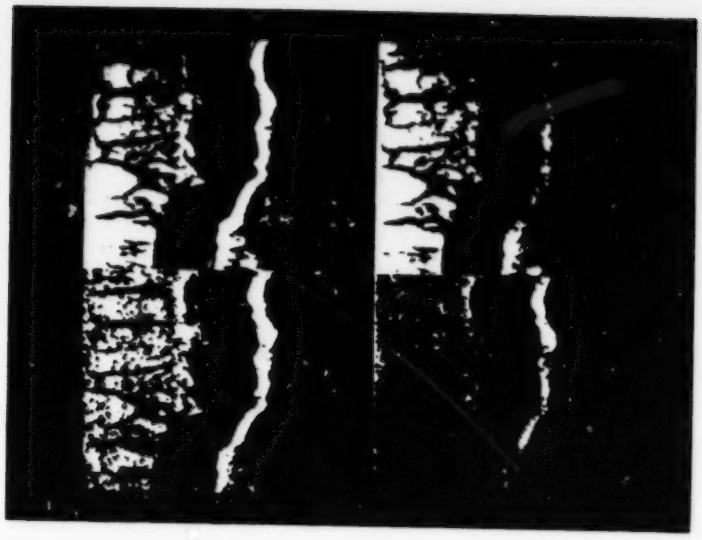


A

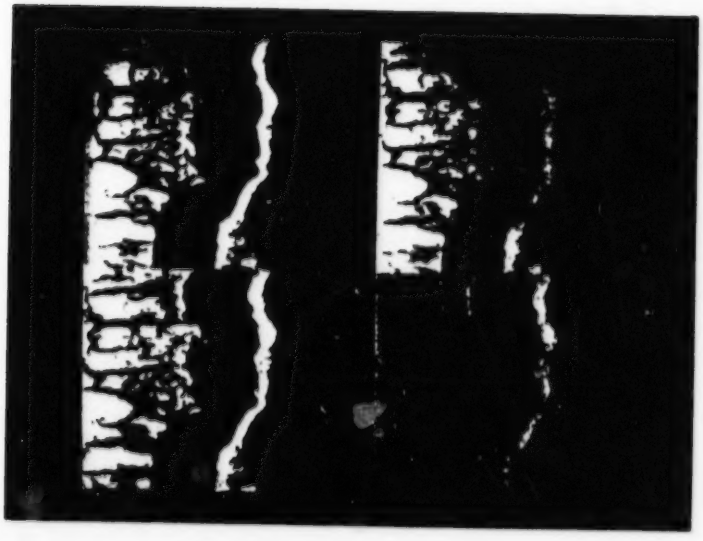


B

Figure 3.5 Port Colborne: Galvanized Steel Wire Longitudinal Cross-Section
(a) SEM Micrograph of Intact Corrosion Product Layer
(b) SEM Micrograph Illustrating Breakaway of Corrosion Product Layer



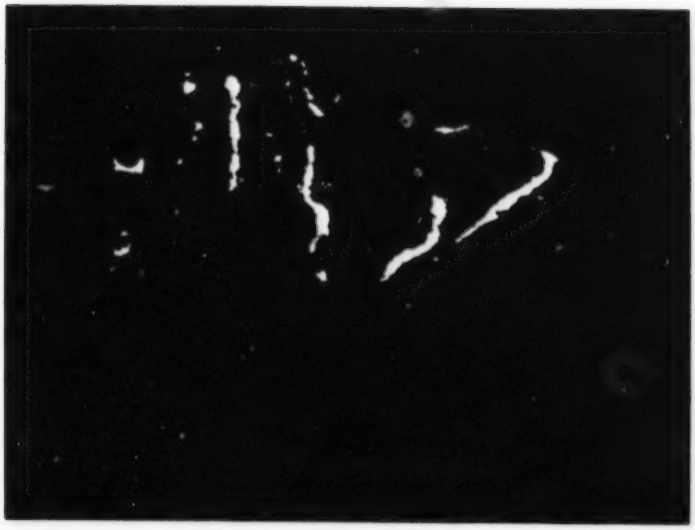
C



D

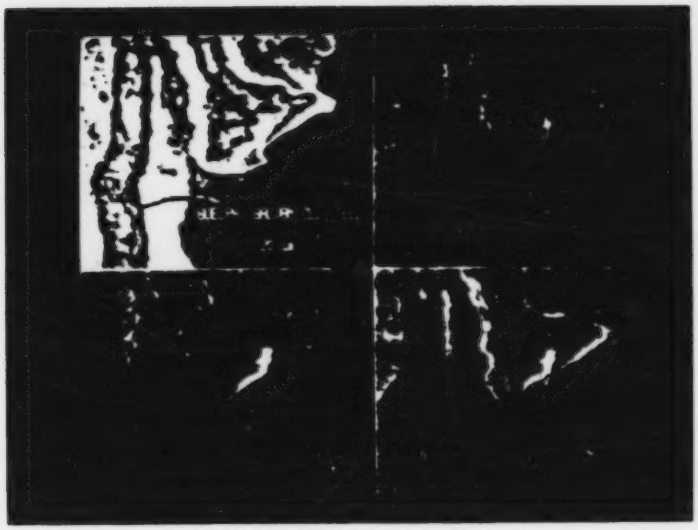
Figure 3.5 Port Colborne: Galvanized Steel Wire
Longitudinal Cross-Section
(c) Elemental Maps (O,Fe,Zn) of
Galvanized Layer
(d) Elemental Maps (O,Cl,Zn) of
Galvanized Layer

A



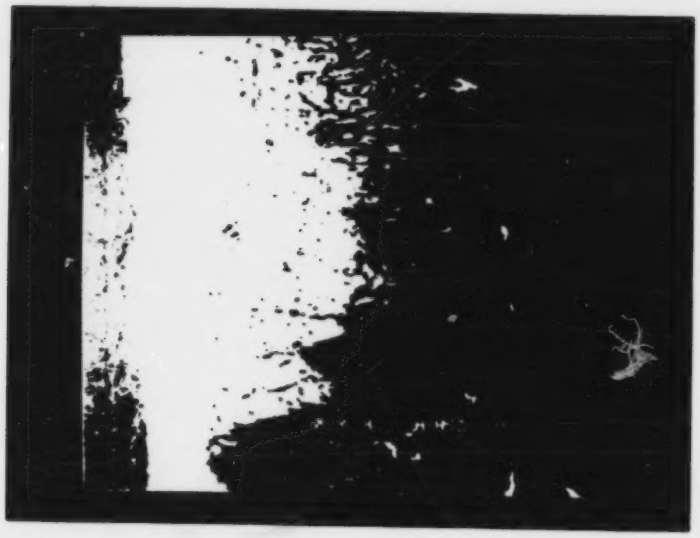
B

Figure 3.6 Guelph: Galvanized Steel Wire
Longitudinal Cross-Section
(a) SEM Micrograph of Corrosion Product Layer
(b) SEM Micrograph of Outermost 50 um of Corrosion Product Layer

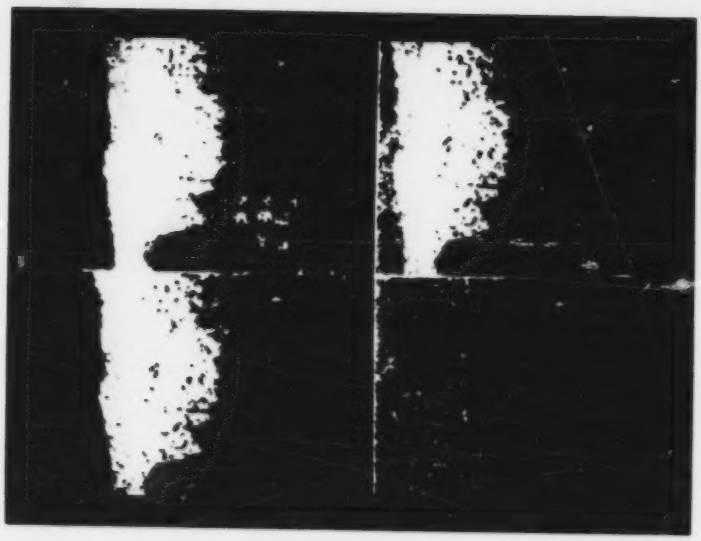


C

Figure 3.6 Guelph: Galvanized Steel Wire
Longitudinal Cross-Section
(c) Elemental Maps (O,Fe,Zn) of
Outermost 50 um of Corrosion Product
Layer

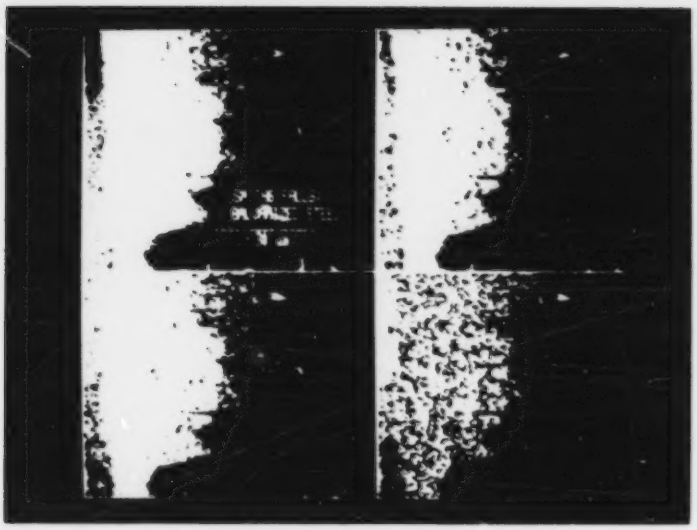


A



B

Figure 3.7 Smiths Falls: Galvanized Steel Wire Longitudinal Cross-Section
(a) SEM Micrograph of Galvanized Layer
(b) Elemental Maps (O,Fe,Zn) of Galvanized Layer



C

Figure 3.7 Smiths Falls: Galvanized Steel Wire
Longitudinal Cross-Section
(c) Elemental Maps (O,S,Zn) of
Galvanized Layer

the presence of amorphous solids of aluminum sulphate (by XRF, EDX), aluminum chloride (EDX) and perhaps zinc hydroxychloride (XRF, EDX). The corrosion product below the oxide crust appears to be amorphous aluminum sulphate as illustrated by Figure 3.2d.

The outer aluminum sample from Smiths Falls shows no evidence of corrosion, other than a passivating film of aluminum oxide, approximately 1 μm thick.

3.1.1.2 Inner Aluminum Strands

The inner aluminum strands from Port Colborne and Smiths Falls are similar in morphology and elemental composition to the respective outer aluminum strands; however, the concentration of sulphur in the amorphous aluminum sulphate of Port Colborne is less (Al/S ~ 18) than that of the outer aluminum strand (Al/S ~ 2). Figures 3.3 and 3.4 are SEM micrographs of inner aluminum samples from Port Colborne and Smiths Falls, respectively. The conductor cable design at Guelph consisted of only a single sheath of outer aluminum strands about a galvanized steel core.

3.1.1.3 Galvanized Steel Strands

The galvanized steel strands from Port Colborne exhibit both buildup and breakaway of approximately 100-150 μm of corrosion product layer (Figures 3.5a and b). Since the original steel-galvanized coating interface is intact, a mechanism involving zinc dissolution, redistribution and then precipitation of corrosion product is suggested. The outermost 100 μm of corrosion product is rich in zinc, sulphur and oxygen (Table 2.8c); however, the innermost layer (30 μm) includes additionally iron and chlorine, but does not include sulphur. Iron is most likely present as an alloy of zinc, introduced during hot dip coating (galvanizing process). The kinetics of zinc hydroxychloride formation may be favourable to sulphate formation.

Zinc loss of the galvanized steel sample from Guelph is extensive such that corrosion of iron has occurred to a depth of 60 μm below the remaining zinc layer, which is less than 25 μm thick (refer to Figure 3.6a). An SEM micrograph at higher magnification of the remaining zinc layer and corresponding elemental maps are displayed in Figures 3.6b and 3.6c, respectively. Alternating layers of iron oxide and zinc oxide further support a mechanism in which dissolution and precipitation of zinc occurs. Energy dispersive x-ray spot analyses of the darker regions in Figure 3.6b have shown chlorine to be present in high concentration, as well (refer to Table 2.8c).

The galvanized steel strand from Smiths Falls, as shown in Figures 3.7a to 3.7c, has a remaining zinc layer between 50 and 60 μm thick and exhibits very little buildup of corrosion product on the aqueous

surface. The corrosion product is shown to be composed of zinc, sulphur, oxygen, and carbon (ie, carbonate by x-ray diffraction). It should be noted that no chlorine has been detected.

3.1.2 Summary of Analytical Results

A summary of the corrosion products of outer aluminum, inner aluminum, and galvanized steel strands from the three locations: Port Colborne, Guelph and Smiths Falls, is presented in Table 3.1. The crystalline structures have been identified by x-ray diffraction (XRD) and the presence of the amorphous products is supported by the results of x-ray fluorescence (XRF) and energy dispersive x-ray analysis (EDX).

TABLE 3.1

CORROSION PRODUCTS

Conductor Sample	Crystalline Products (XRD)					Amorphous Products (XRF, EDX, Auger Spectroscopy)
	$Al(OH)_3$	$ZnSO_4$	$Zn(OH)_2$	$FeO(OH)$	$Zn_4Al_2(OH)_6CO_3 \cdot 4H_2O$	
Outer Aluminum:						
Port Colborne	X	-	-	-	-	Aluminum hydroxysulphate Aluminum hydroxychloride Zinc hydroxychloride
Guelph	-	-	-	-	-	Aluminum hydroxysulphate Aluminum hydroxychloride Zinc hydroxychloride Carbonaceous surface layer
Smiths Falls	-	-	-	-	-	Carbonaceous surface layer
Inner Aluminum:						
Port Colborne	X	-	-	-	-	Aluminum hydroxysulphate
Smiths Falls	-	-	-	-	-	-
Galvanized Steel:						
Port Colborne	X	X	X	-	-	Zinc hydroxysulphate Zinc hydroxychloride
Guelph	-	-	-	X	-	Zinc hydroxysulphate Zinc hydroxychloride
Smiths Falls	-	-	-	-	X	Zinc hydroxysulphate
Loose Deposits:						
Port Colborne	- $Al(OH)_3$, (corrosion product), NiO, $CaSO_4$, also sulphate, chloride, nitrate, fluoride.					

In addition to the corrosion products listed above, NiO was detected on the Port Colborne strands of aluminum and galvanized steel; and quartz, and quartz and feldspar deposits were present on the Guelph and Smiths Falls conductors, respectively. These loose deposits, as well as the black deposits on the Guelph and Smiths Falls aluminum conductors, which are carbonaceous in origin are believed to be suspended particulates of the local environment, and are to be distinguished from corrosion products. All aluminum conductor samples were shown to contain fairly significant concentrations of iron and zinc, by x-ray fluorescence. Redistribution of zinc salt precipitates and iron oxides from the corroding galvanized steel samples is probably partly responsible; however, in the case of Smiths Falls samples in which there is limited corrosion, the source of iron and zinc may be contamination by the steel instrument used to scrape and sample the surface layers.

Amorphous aluminum hydroxysulphate is believed to be the predominant corrosion product of aluminum conductors located at Port Colborne and Guelph, but not of the sample from Smiths Falls. It appears that this product is saturated with sulphate, as shown in Figure 3.1c, at Al/S approximately equal to 2. Amorphous aluminum sulphates of the form, $Al_x(SO_4)_y \cdot (OH)_z$, are also reported in the literature [5,6,7,8] and basic aluminum sulphates formed outdoors have been reported predominantly amorphous. This observation is supported by the fact that it is statistically disfavourable to assemble numerous naturally-occurring constituents and that rapid outdoor temperature changes do not allow sufficient time for crystalline rearrangement [5]. A complex zinc-hydroxy-chloro-sulphate hydrate $\{Zn_{12}(OH)_{15}(SO_4)_3Cl_3(H_2O)_5\}$ has also been identified following exposure tests to concentrated sulphate-chloride salt spray [9].

In this study, amorphous zinc hydroxysulphate is believed to be present in the galvanized steel samples from all three locations. Biestek and co-workers [10] have found that amorphous zinc hydroxysulphates, $Zn_{y+1}(SO_4)(OH)_{2y} \cdot 4H_2O$, are the only stable species present in zinc corrosion layers after extended exposures.

Chlorides, most likely amorphous aluminum hydroxychloride and zinc hydroxychloride, were detected in the aluminum and steel strands, respectively, from Port Colborne and Guelph. The aluminum chloride corrosion product appeared as a crust and was present most noticeably on the interior surface of outer aluminum strands situated at Port Colborne (Al/Cl approximately 2). It should be noted that the solubility of chloride products would prevent large buildups of chloride surface species on the exterior surface exposed to precipitation. Specific compounds containing chlorine and aluminum have not yet been identified on aluminum surfaces exposed to outdoor atmospheres [5]; however, $AlCl_3$ and intermediate aluminum hydroxychlorides, $AlCl(OH)_2 \cdot 4H_2O$, have been observed in the laboratory [11].

The amorphous zinc hydroxychloride corrosion product was found deep (innermost 15 μm in Figure 3.5d) in the corrosion layer of the galvanized steel strands from Port Colborne, unlike the hydroxysulphate. Only highly concentrated spots of chloride product were detected in the Guelph sample (Table 2.8c). The mixed salt, $Zn_5(OH)_8Cl_2$, has been found in samples exposed to industrial atmospheres [10] and marine atmospheres [6]. Since zinc hydroxychlorides are soluble in weak acid solutions, they would be present only if isolated from the often acidic aqueous surface layer, ie, deep within the corrosion layer. An alternate suggestion by Biestek [10] is that hydroxychlorides are formed rapidly, upon exposure, but are gradually transformed into less soluble hydroxysulphates.

Chloride species were not detected in the conductor samples from Smiths Falls.

Crystalline aluminum hydroxide ($Al(OH)_3$) was detected on the surfaces of the Port Colborne conductor samples. A study by Friel [6] has shown $Al(OH)_3$ to be present in marine environments but not industrial environments; and thus, to be associated with chloride salts. Aluminum hydroxide may not have been detected in the Guelph sample due to breakaway of the corrosion product layer as shown in Figure 3.2a.

The presence of FeO(OH) on the galvanized steel strands from Guelph confirms failure of the zinc coating. In contrast, hydroxide and carbonate products on galvanized steel strands located in Port Colborne and Smiths Falls, respectively, are stable at near-neutral pH and are known to be passivating. Zinc hydroxide ($Zn(OH)_2$) and mixed salt hydrozincites (e.g., $Zn_4Al_2(OH)_{16}CO_3 \cdot 4H_2O$) predominate under conditions of dew or adsorbed water vapour [12]. These passivating layers have offered significant protection against corrosion since the respective ages of the Guelph, Port Colborne, and Smiths Falls conductors are 46.9, 64.0 and 60.8 years and yet, negligible corrosion is observed for the Smiths Falls sample.

3.2 Corrosion Mechanisms

A review of the literature identifying the atmospheric pollutants, the reactions and the meteorological conditions responsible for corrosion has been conducted [13]. The amorphous and crystalline corrosion products, determined in the present study, have led to further insight of the mechanisms by which corrosion of aluminum and galvanized steel strands of transmission line conductors, is effected. The results are consistent with the following reaction mechanisms.

Under moist conditions, zinc is readily oxidized to zinc hydroxide:

$$2Zn + H_2O + 1/2\ O_2 \rightarrow 2Zn(OH)_2.$$

At fairly neutral pH (6-8) and in the presence of carbon dioxide, zinc hydroxide reacts to form zinc hydroxycarbonate [14]. Alternatively, a mixed salt hydrozincite such as $Zn_4Al_2(OH)_{16}CO_3 \cdot 4H_2O$ may form, as in the case of the Smiths Falls galvanized steel strand which was in contact with aluminum wire. Pollutant constituents may further react to form zinc hydroxysulphates and hydroxychlorides, as in the samples from Port Colborne and Guelph. Amorphous zinc hydroxysulphate is also believed to be present on the galvanized steel strands from Smiths Falls.

$$Zn(OH)_2 + 0.5CO_2 \quad \text{-->} \quad ZnOH(CO_3)_{0.5} + 0.5H_2O$$
$$xZn(OH)_2 + zSO_2 + (2z+y-x)/2\ O_2 \quad \text{-->} \quad Zn_x(OH)_y(SO_4)_z + xH_2O$$
$$xZn(OH)_2 + zCl^- + (2x-y)\ H^+ \quad \text{-->} \quad Zn_x(OH)_yCl_z + (2x-y)\ H_2O.$$

These products can protect the surface from further attack; however, in the presence of moisture of low pH, they may dissolve to form zinc sulphate, as was evidenced by the Port Colborne galvanized steel samples.

$$Zn + SO_2 + O_2 \quad \text{-->} \quad ZnSO_4$$
$$Zn(OH)_2 + SO_2 + 1/2\ O_2 \quad \text{-->} \quad ZnSO_4 + H_2O$$
$$Zn(OH)(CO_3)_{1/2} + SO_2 + O_2 + 2H^+ \quad \text{-->} \quad ZnSO_4 + 3/2\ H_2O + 1/2\ CO_2.$$

As the reactions proceed, the pH increases until a basic salt precipitates (eg, carbonate) which inhibits further corrosion until additional acid is supplied. Thus, alternating destruction and buildup of the protective film occurs [15] and a corrosion layer nonuniform in depth and composition results. The galvanized steel strands from Guelph showed alternating layers of zinc and iron products rich in oxygen, and the samples from Port Colborne exhibited corrosion products in which the outer layers were concentrated in sulphate and chloride, and the innermost layers in chloride only (Table 2.8c and Figure 3.5d). These compositions may result from the effect of changing acidic media on solubilities; however, reaction kinetics and selective ion mass transport through corrosion precipitates must also be considered. For example, Sato [16] discusses a case in which the corrosion precipitate film is anion-selective (eg, chloride-selective). As anodic corrosion proceeds under the precipitate film, the inside occluded aqueous solution becomes enriched in both metal ion and chloride ion. The resulting acidification, due to hydrolysis of the concentrated metal chloride, and the electro-osmotic migration of H_2O through the precipitate film to the occluded solution provide conditions favourable for localized corrosion of the underlying metal.

Since zinc sulphate is soluble and is easily washed away by rain, no protection is offered by this corrosion product and the rate of corrosion is high. Almost complete dissolution of the zinc coating was evidenced by the galvanized steel samples from Guelph. In the corrosion of zinc, Barton [17] assumes that the formation of zinc sulphate from zinc hydroxide is the rate-determining step and suggests

that the sulphate and/or chloride bound at the corrosion product/air boundary acts as a corrosion stimulator. The corrosion of zinc is then proportional to the pollutant levels of sulphate and chloride in contact with the surface. The rather limited environmental data available in Table 2.3, does suggest there is a correlation between degree of corrosion and sulphur dioxide and chloride concentrations.

Table 2.3 also indicates that the concentrations of total suspended particulates (TSP) follow the relative corrosion intensities of the three conductor samples. Total suspended particulates include sulphates and chlorides, which have been identified as the most aggressive species [18], as well as, the carbonaceous deposits detected by Auger spectroscopy (Table 2.6). Carbon has been shown to play an important role in the corrosion mechanism by absorbing sulphur oxides and concentrating them at the surface of the metal [19]. In addition, differential oxygen (aeration) cells may be established where carbon deposits act as cathodes to the aluminum anode. Since carbon deposits are detected on both Guelph and Smiths Falls conductors, yet corrosion is much more extensive at the Guelph site, other factors, such as the availability of electrolyte are crucial factors. Although the relative humidity values, listed in Table 2.3, give an indication of surface wetness, the periods over which the relative humidity is greater than a threshold amount (eg, 80% RH [20]) might be a better measure of electrolyte availability.

It is well known that aluminum exposed to the atmosphere is covered with a dense, thin oxide coating (10-20 nm thick) which serves as a protective barrier to corrosion [14]. However, anions such as SO_4^{2-} or Cl^- may deposit on the oxide surface to form water-soluble salts or may be incorporated in the lattice to form a variety of basic salts and complexes. Chloride corrosion products were detected on the Guelph sample (Figure 3.2b), as well as on the interior surface (which is isolated from precipitation) of outer aluminum strands from Port Colborne (Table 2.8a: Al/Cl approximately 2). Aluminum conductors from both sites formed amorphous aluminum sulphates, for which an Al/S saturation ratio of 2 was observed (Table 2.8a). The results of this study are consistent with the stages of aluminum corrosion described by Foley [21]: (i) adsorption of reactive anions (eg, Cl^-, SO_4^{2-}) on the oxide-covered aluminum; (ii) chemical reaction with the aluminum oxide lattice or precipitated aluminum hydroxide; (iii) thinning of oxide film by dissolution; and then, (iv) direct attack of the exposed metal by the anion. In addition, corrosion of aluminum occurs principally at mechanical flaws or grain boundaries and manifests itself as deep pits rather than uniform deterioration [22].

Laboratory studies of aluminum attack in concentrated sulphate and chloride solutions have indicated that the average corrosion rate is higher in high-sulphate solutions, however, deeper pits result in high-chloride solutions [9]. The localized pitting of aluminum by chloride ion is fairly well understood [23]. Following penetration of the oxide

film by chloride ion, aluminum ions go into solution and decrease the local pH. In concentrated chloride solution, aluminum chloride ($AlCl_3$) is known to form, and in the presence of water, the corrosion product is converted to hydroxide ($Al(OH)_3$) [24]. Obvious intermediates are aluminum hydroxychlorides which have been identified in laboratory experiments [25]. In support of this mechanism, Friel [6] has found that bayerite ($Al(OH)_3$) forms in marine environments only, after 9 years of exposure. In the present study, bayerite was detected on the Port Colborne outer aluminum strands only; however, the Guelph samples did experience breakaway and this may account for the absence of $Al(OH)_3$. The samples from Smiths Falls did not form chloride corrosion products and thus, would not be expected to form bayerite.

3.3 Effects of Environmental Factors

In order for metal corrosion to occur, an anodic reaction, such as metal dissolution or oxide formation, and a cathodic reduction, such as proton or oxygen reduction must proceed simultaneously via an ionically conductive electrolyte. Aqueous corrosion is a complicated process which is affected by many variables including the composition and metallurgical properties of the metal or alloy and the chemical (composition) and physical (temperature, conductivity) properties of the environment.

The chemical compositions of the corrosion products in this study indicate that chloride and sulphate pollutants are corrosive towards metals and also contribute to the overall conductivity of the surrounding electrolyte. Other electrolyte properties include availability and wettability. The availability of an electrolyte is a function of relative humidity or more precisely, the period over which the relative humidity is greater than a threshold value (eg, 80%). In addition, some corrosion products are deliquescent (eg, chlorides) and further increase the time of wetness. Wettability, on the other hand, is measured by the surface tension of the electrolyte and is a function of chemical composition and temperature. Ammonium salt solutions are known to have low surface tensions and thus, exhibit good wetting behaviour [9]. Although surface tension as well as ionic conductivity increase with temperature, a loss in electrolyte due to evaporation will also occur. Studies have shown that corrosion rate of zinc in moist air (Relative Humidity > 80%) reaches a maximum at -2°C [26].

Formation and stability of corrosion products which passivate the metal from further attack (eg, Al_2O_3, $ZnCO_3$, $Zn_4Al_2(OH)_{14}CO_3 \cdot 4H_2O$, and to some extent, zinc hydroxychloride, zinc hydroxysulphate) are dependent on the supply of CO_2, in the case of carbonate formation, and also on the acidity of the electrolyte media. Both aluminum and zinc form protective coatings at neutral pH; in acidic media, the corrosion process is dependent on the anion present (eg, Cl^-, SO_4^{2-}) as discussed

in Section 3.2, Corrosion Mechanisms. The amount of precipitation also plays a role in the dissolution of protective layers; however, dissolution of aggressive products occurs as well.

Finally, it has been observed that the relative degree of corrosion of the conductors from the three location is as follows: Guelph > Port Colborne > Smiths Falls. It appears that the limited corrosion at the Smiths Falls site can be attributed to lower acidity, lower chloride concentration in precipitation and lower relative humidity. Chloride corrosion products were not detected on the aluminum nor galvanized steel strands of Smiths Falls, and a basic carbonate product, passivating in nature, was present on the galvanized steel wires. Since environmental data are lacking, it is difficult to compare the deterioration of the galvanized coatings at Port Colborne and Guelph in terms of pollutant levels. Once results of field studies conducted at the sites are known, a more comprehensive discussion of environmental parameters can be issued.

4.0 CONCLUSIONS

1. A test procedure involving x-ray diffraction analysis, scanning electron microscopy with energy dispersive x-ray analysis facilities and other spectroscopic techniques (x-ray fluorescence, Auger spectroscopy) is suitable for the identification of corrosion products of ACSR transmission line conductors.

2. Aluminum wires exposed to industrial environments (Guelph, Port Colborne) for greater than 45 years, form amorphous aluminum sulphates and chlorides. Bayerite ($Al(OH)_3$) is detected in some cases. Aluminum wires exposed to rural environments (Smiths Falls) for 60 years show no evidence of corrosion other than a passivating layer of aluminum oxide, approximately 1 μm thick.

3. Galvanized steel strands sheathed by aluminum form amorphous zinc hydroxysulphates in both rural and industrial environments; however, amorphous chlorides are present only in industrial environments (Port Colborne, Guelph). Zincite ($Zn_4Al_2(OH)_{14}CO_3 \cdot 4H_2O$) appears to passivate surfaces as in the rural Smiths Falls site; and to a limited extent, $Zn(OH)_2$, offers protection at Port Colborne. Zinc sulphate is also detected on Port Colborne wires. The presence of FeO(OH) and substantial breakaway of corrosion product layers indicate failure of the galvanized coating at the Guelph site.

4. Corrosion of aluminum prior to interaction with atmospheric corrodents involves formation of an oxide/hydroxide surface layer. Subsequent corrosion occurs preferentially at mechanical flaws or grain boundaries. Amorphous aluminum sulphate is the predominant corrosion species; however, pronounced localized pitting is known to be effected by chloride ions.

5. Under moist conditions, zinc is readily oxidized to zinc hydroxide, which forms zinc hydroxycarbonate and mixed salt hydrozincites in the presence of CO_2. Pollutant constituents may further react to form amorphous sulphates and chlorides. Under changing acidic conditions, these products dissolve, and precipitate other zinc salts such that a corrosion layer nonuniform in depth and composition results.

6. The chemical compositions of the corrosion products identified in this study indicate that chloride and sulphate pollutants are aggressive towards aluminum and zinc metal surfaces and contribute to the overall conductivity of the surrounding electrolyte. The effectiveness of the electrolyte, which is crucial for ionic transfer during electrochemical reactions of corrosion, is determined by the prevailing relative humidity, the amount of precipitation, and temperature and chemical composition which influence conductivity and wetting behaviour. Finally, acidic conditions are known to adversely affect the stability of passivating corrosion product layers of aluminum and zinc.

5.0 RECOMMENDATIONS FOR FUTURE STUDIES

Pollutants which are responsible for atmospheric corrosion of ACSR transmission line conductors have been identified in this study; however, a correlation equation between the degree of corrosion, as measured by mechanical properties or Cormon rating, and an environmental corrosion index will be useful in predicting the remaining life of a conductor. An environmental corrosion index may be computed with a suitable algorithm which considers key environmental parameters.

Dispersion modelling studies should also be pursued to predict pollutant levels in the vicinity of sources (eg, highway, lime plant) and in areas remote from environmental monitoring stations. These results may be used to refine correlation equations.

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